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Effect of acetic acid addition on chemical conversion of woods as treated by semi-flow hot-compressed water

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Abstract

Effect of acetic acid (AcOH) addition on chemical conversion of Japanese beech (*Fagus crenata*), as a hardwood, and Japanese cedar (*Cryptomeria japonica*), as a softwood, was investigated in the course of treatment in a semi-flow reactor with hot-compressed water (H-CW). One-step treatment of Japanese beech was preliminarily performed to examine the effect of AcOH concentrations on the decomposition behavior at 150–290°C/10 MPa/30 min. Based on the obtained results, two-step semi-flow H-CW treatment with 1 wt% AcOH at 210°C/10 MPa/15 min (1st stage) and 260°C/10 MPa/15 min (2nd stage) was thus selected as the most appropriate treatment and a comparative study of the two woods was accordingly conducted. The differences in decomposition behavior observed between the two woods clearly proved that the addition of AcOH played an important role in enhancing the hydrolysis and decomposition of cell wall components in Japanese cedar due to the lesser amount of acetyl residue in softwood hemicelluloses and its lignin structure.

Keywords: acetic acid; chemical conversion; hardwood; hot-compressed water; hydrolysis; Japanese beech; Japanese cedar; softwood.

Introduction

Acetic acid (AcOH) process has long been known as an effective method for delignification in the pulp and paper industry (Nimz and Casten 1986; Sano et al. 1989, 1990; Pan et al. 1998). This particular process is generally conducted under the conditions: 105°C; atmospheric pressure or above; 0.5–4 h; AcOH aqueous solution 90%–95%; mineral acid catalyst (e.g. HCl or H_2HO_4) 0.1%–4% (Sano et al. 1990; Parajó et al. 1993; Pan and Sano 2005). Cellulose, hemicelluloses, and lignin in lignocellulosic materials can be dissolved and degraded under these conditions. The obtained AcOH pulp is composed mainly of cellulose, which possesses a comparable physical strength to the conventional pulps for papermaking. Acetic acid lignin can serve as feedstocks for many value-added lignin products due to its lower molecular weight and higher reactivity. In addition, the sugars from hemicelluloses are readily convertible to chemicals and fuels (Pan and Sano 2005).

Recently, we have conducted a two-step hydrolysis of Japanese beech (*Fagus crenata*) and Japanese cedar (*Cryptomeria japonica*), in the course of which the woods are treated in a semi-flow reactor with hot-compressed water (H-CW) at 230°C/10 MPa/15 min (1st stage) and 270–280°C/10 MPa/15–30 min (2nd stage) (Lu et al. 2009; Phaiboonsilpa et al. 2009, 2010a,b; Saka et al. 2009). In such studies, a substantial production of decomposed compounds was realized in the 2nd stage due to its relatively high treatment temperature. These decomposed compounds can end up with loss of saccharides, and inhibitory effect can occur on the subsequent fermentation step resulting in a lower yield of ethanol.

This earlier finding prompted the necessity for our further study to lessen the decomposed compounds by means of reducing the treatment temperature. Addition of AcOH into the reaction mixture was an alternative to achieve this goal; in addition, the presence of AcOH presents no drawback to the subsequent process steps in our newly-developed eco-ethanol production process via AcOH fermentation and hydrogenolysis (Saka et al. 2009).

In this paper, therefore, the effect of AcOH addition on chemical conversion of Japanese beech (as a hardwood) and Japanese cedar (as a softwood) in H-CW treatment will be investigated. The most appropriate treatment conditions for the hydrolysis of hemicelluloses and cellulose are sought, whereby the production level of decomposed compounds should be minimized.

Experimental

Materials

Extractives-free wood samples of Japanese beech (*Fagus crenata*) and Japanese cedar (*Cryptomeria japonica*) were prepared according to the method described by Lu et al. (2009) and Phaiboonsilpa et al. (2009, 2010a). Chemical composition of the wood samples are described in the quoted papers. All chemicals were of reagent grade and used without purification.

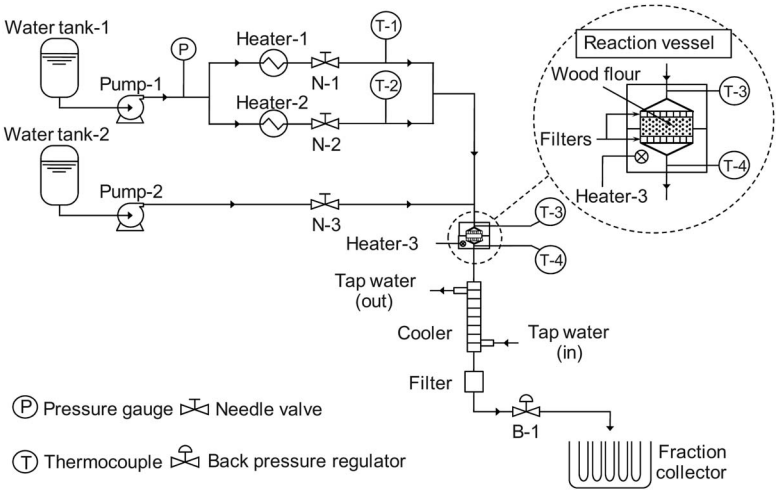

Figure 1 Schematic diagram of the semi-flow H-CW treatment system used in our studies.

H-CW treatment and fractionation of the products

Figure 1 illustrates a schematic diagram of the semi-flow H-CW treatment system used in our studies. Its detailed operational procedures were described by Lu et al. (2009). Instead of distilled water, 0.1, 1, and 3 wt% AcOH aqueous solutions were prepared and stored in water tank-1. Approximately 0.5–1 g of extractives-free wood flour was placed in the reaction vessel and treated by H-CW + AcOH at a flow-rate of 10 ml min^{-1}.

Solubles in H-CW were collected and left at the ambient temperature and pressure for 12 h. After being filtrated over a 0.45-μm membrane, the water-soluble portion was then subjected to subsequent analyses. The solid residue remaining in the reaction vessel after the treatment was oven-dried and analyzed.

As a preliminary study, Japanese beech was treated by one-step semi-flow H-CW + AcOH (0.1%, 1%, and 3%) at temperatures between 150–290°C; pressure 10 MPa; time 30 min. The best conditions found were employed in the subsequent two-step treatment.

Analyzes of products

Acetic acid was removed from the water-soluble portion by freeze-drying. Distilled water was then added to adjust its volume back to the initial stage. The AcOH-free samples were then analyzed by HPAEC, HPLC, and capillary electrophoresis (CE) as described by Lu et al. (2009) and Phaiboonsilpa et al. (2010a). All the product percentages were presented on oven-dried weight basis of the extractives-free wood flour.

The Klason lignin determination was performed according to Dence (1992) and Minami and Saka (2003). The crystallographic structure of cellulose was characterized by X-ray diffractometry.

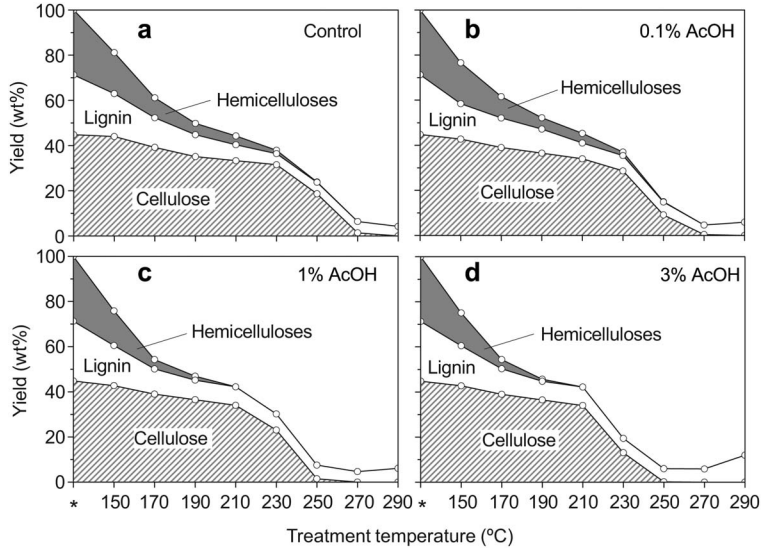

Figure 2 Change in chemical composition of Japanese beech residues as treated in a semi-flow reactor with hot-compressed water at 150–290°C/10 MPa/30 min. (a) Without AcOH (control), (b) 0.1% AcOH, (c) 1% AcOH, and (d) 3% AcOH. Asterisks (*) denote the composition of untreated wood.

Apparent crystallinity was estimated as the method described by Segal et al. (1959).

Results and discussion

Effect of AcOH addition

Figure 2 shows changes in chemical composition of Japanese beech residues as treated by one-step semi-flow H-CW with 0.1%, 1%, and 3% AcOH at 150–290°C/10 MPa/30 min. For comparison, the treatment without AcOH addition is presented in Figure 2a. The results clearly demonstrate that hemicelluloses and cellulose are liquefied completely in the presence of AcOH at lower temperatures. Higher acid concentrations display a greater decomposition degree. On the other hand, as a result of acid addition, no such a significant difference in lignin decomposition was observed at 150–250°C. At a higher temperature, however, the residual lignin was increased. The most pronounced effects can be seen in the treatment with 3% AcOH at 290°C (Figure 2d). This observation might be attributed to the condensation reaction of lignin.

As recognized in the literature (Davis et al. 1986; Parajó et al. 1995; Vázquez et al. 1997), the decomposition behavior of lignin can be satisfactorily explained by a model corresponding to dissolution followed by condensation and re-precipitation of the lignin onto the lignocellulosic matrix. It was also reported by the same authors that the selectivity of lignin condensation became dominant when the treatment severity was high enough. Therefore, the lignin condensation observed in this present study can be confirmed.

From Figure 3a, it is clear that changes in Japanese beech residues do not show a great difference for all the treatments at temperatures between 150 and 210°C, where hemicelluloses were mainly hydrolyzed whereas lignin and cellulose were decomposed in part (see Figure 2). Nonetheless, those changes in the treatment with AcOH varied more apparently at 210–270°C. In this temperature range, hemicelluloses were already removed from the system and only cellulose and lignin were subjected to the treatment. As seen from Figure 2, lignin is likely to be decomposed at the same degree over this temperature range. Therefore, the differences observed at 210–270°C are mainly attributable to the cellulose decomposition.

These results can be explained by the different chemical composition of hemicelluloses, which contain not only various polysaccharides but also acetyl and uronic acid groups. These acids can be liberated in the course of hydrothermal treatment and serve as a catalyst in hydrolysis, a process, which is known as autohydrolysis (Lora and Wayman 1978; Laser et al. 2002). For this reason, the additional AcOH does not show a significant effect on improving the hydrolysis of hemicelluloses in the case of the hardwood Japanese beech.

Figure 3b, moreover, demonstrates that the crystalline structure of cellulose could be readily destroyed at lower temperatures in presence of AcOH, and higher acid concentrations increase the effect. At 150°C, however, the crystallinity was elevated. This can be explained by an effective removal of amorphous moieties of the cell wall—i.e., lignin and hemicelluloses—with the assistance of the additional AcOH at a relatively low temperature.

Hydrolyzed products from hemicelluloses and cellulose

Figure 3c shows the production of xylo- and cello-saccharides from Japanese beech after a one-step H-CW treatment in a semi-flow reactor in presence of AcOH at 150–290°C. Evidently, the acid addition does not help significantly to increase the yields of xylo-saccharides. However, an excessive decomposition of the hydrolyzed products of hemicelluloses can be observed, as seen on the yields at 210°C. As for cello-saccharides, although higher yields could be attained at even lower temperatures in presence of AcOH.

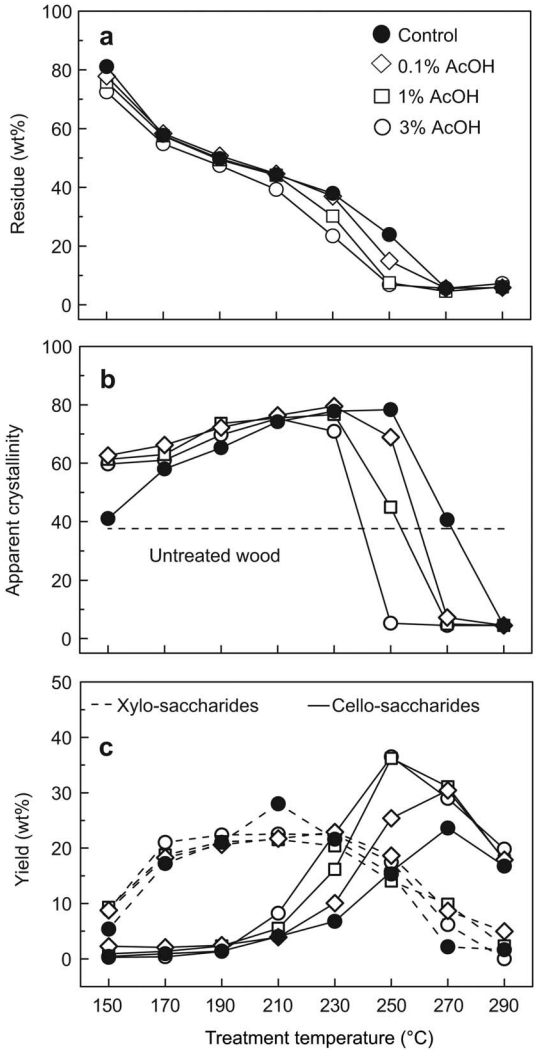

Figure 3 Change in yield (a) and apparent crystallinity (b) of wood residues, and production of saccharides (c) from Japanese beech after treatment in a semi-flow reactor with hot-compressed water with 0%, 0.1%, 1%, and 3% AcOH at 150–290°C/10 MPa/30 min.

The difference with respect to the hydrolysis behaviors between hemicelluloses and cellulose is also obvious here.

Based on the previous results, the parameters 210°C/10 MPa/15 min were chosen for the 1st stage. As seen from Figure 3c, the substantial increases in cello-saccharide yields could be obtained at 250°C in presence of 1% and 3% AcOH. To minimize the corrosion effect, 1% acid concentration was preferred. However, Figure 3b indicates that cellulose crystallinity seems to be drastically destroyed at temperatures higher than 250°C with 1% AcOH. Therefore, the parameters 260°C/10 MPa/15 min with 1% AcOH were thus set as tolerable conditions for the 2nd stage.

Two-step treatment with/without acetic acid

Various products from Japanese beech and Japanese cedar are summarized in Table 1, which were obtained by a two-step H-CW treatment in a semi-flow reactor with 1% AcOH, with 1st step 210°C/10 MPa/15 min and 2nd step 260°C/10 MPa/15 min.

In the case of Japanese beech, hydrolyzed products from hemicelluloses are as follows: xylo-saccharides—such as xylose and xylo-oligosaccharides—mannose, galactose, arabinose, rhamnose, glucuronic acid and methanol. Those of Japanese cedar are glucomanno-saccharides—such as mannose, glucose and oligomeric glucomannan—galactose, xylo-saccharides—such as xylose and xylo-oligosaccharides—arabinose, glucuronic acid and methanol. Hydrolyzed products from cellulose include cello-saccharides—such as glucose and cello-oligosaccharides—and fructose, as an isomerized product from glucose. Total amounts of lignin-derived products are estimated from the lignin content in the original wood meal and that in the solid residue after the H-CW treatment.

Dehydrated compounds include levoglucosan, 5-hydroxymethylfurfural (5-HMF) and furfural; fragmented compounds refer to erythrose, methylglyoxal and glycolaldehyde; and organic acids are lactic, glycolic and formic acids. Unknown product can be calculated as follows: unknown = 100%-total recovery product yields (%)-residue (%).

From Table 1, it is visible that the two-step treatment with 1% AcOH could be performed at temperatures 10–20°C lower than those of the treatment without acid addition, while similar product yields were obtained. Namely, 230°C (1st stage) and 270°C (2nd stage) could be reduced to 210°C and 260°C, respectively. In total, 93.7% and 92.2% of Japanese beech were solubilized in H-CW with and without AcOH. As for Japanese cedar, the soluble portion increased from 82.3% to 83.7% as a result of the acid addition. The rest of around 6%–8% of Japanese beech and 12%–14% of Japanese cedar were left as solid residues composed mainly of lignin, conversion products of polysaccharides, and cellulose incompletely hydrolyzed. The yield of residues was higher in the case of Japanese cedar, due to its higher lignin content and the higher portion of less soluble condensed-type linkages of guiacyl units in its (softwood) lignin.

The catalytic effect of AcOH for delignification of both woods is obvious. However, the acid addition is less effective to increase the hydrolyzed products from hemicelluloses and cellulose for Japanese beech. In case of Japanese cedar, on the other hand, the acid addition has a significant effect on the hydrolysis of hemicelluloses and cellulose.

Table 2 is a compilation of molar ratios between sugar and acid residues in the major hardwood and softwood hemicelluloses according to Timell (1967). As demonstrated here, softwood hemicelluloses possess less acetyl group than that of hardwoods. This is the reason why additional AcOH plays

Table 1 Comparison of various products from Japanese beech and Japanese cedar as treated by two-step semi-flow hot-compressed water (1st 230°C/10 MPa/15 min and 2nd 270°C/10 MPa/15 min) and two-step semi-flow hot-compressed water with 1 wt% AcOH (1st 210°C/10 MPa/15 min and 2nd 260°C/10 MPa/15 min)[a-c].

	Yield (wt% on extractives-free wood basis)								
	Hot-compressed water-soluble portion							Residue	
Two-step hot-compressed water treatment	Hydrolyzed prod. from hemicelluloses	Hydrolyzed products from cellulose	Lignin-derived products	Dehydrated compounds	Fragmented compounds	Organic acids	Unknown	Lignin	Saccharides[a]
Japanese beech									
Without AcOH	28.7 (*100.0*)[b]	28.1 (*62.7*)	19.9 (*76.8*)	2.0	0.7	0.8	12.0	6.0 (*23.2*)	1.8 (*4.0*)
With 1% AcOH	28.1 (*97.9*)	29.7 (*66.3*)	21.0 (*81.1*)	2.8	1.0	1.1	10.0	4.9 (*18.9*)	1.4 (*3.1*)
Japanese cedar									
Without AcOH	18.9 (*100.0*)	31.2 (*64.6*)	18.8 (*58.2*)	1.9	2.4	0.4	8.7	13.5 (*41.8*)	4.2 (*8.7*)
With 1% AcOH	22.2 (*116.2*)	44.1 (*91.3*)	19.6 (*60.7*)	2.0	2.5	0.4	ND[c]	12.7 (*39.3*)	3.6 (*7.5*)

[a]Saccharides from incompletely-hydrolyzed cellulose.
[b]Italic values in parentheses indicate relative % of products from hemicelluloses, cellulose, and lignin compared to their contents in original extractives-free wood flour.
[c]ND, not determined.

Table 2 Comparison of molar ratio between sugar and acid residues in the major hardwood and softwood hemicelluloses (Timell 1967).

Hardwood hemicelluloses (*O*-acetyl-*O*-methylglucuronoxylan)		Softwood hemicelluloses (*O*-acetyl-galactoglucomannan)	
Residue	Molar ratio	Residue	Molar ratio
Acetic acid	10	Acetic acid	0.24
Glucuronic acid	1	Galactose	0.1–1
Xylose	7	Glucose	1
		Mannose	3

an important role in enhancing the hydrolysis of cell wall components in Japanese cedar.

Based on the configuration of semi-flow system, liberated AcOH and other organic acids from the hydrolysis in the 1st stage were flushed from the reaction vessel. As a consequence, the acids cannot serve as catalysts in the 2nd stage, where only cellulose and remaining lignin were left. The effect of AcOH addition is nearly identical at this stage for both woods. However, additional AcOH might help improve cellulose hydrolysis by reacting with softwood lignin, but a clear explanation for this observation cannot be given at this moment.

The hydrolyzed saccharides from both woods were recovered to a higher extent in monomeric form in the presence of AcOH (Table 3). Glucose and its oligosaccharides are derived mainly from cellulose during hydrolysis in the 2nd stage, while the other saccharides are from hemicelluloses in the 1st stage. Fructose is a result of isomerization of glucose. It is obvious that the additional AcOH can promote the hydrolysis of soluble oligosaccharides obtained in both stages.

More extensive decomposition reactions occur in the presence of AcOH, as indicated by the higher yields of dehydrated and fragmented compounds, as well as organic acids (Table 1). The two-step process with H-CW in the presence of AcOH needs more optimization.

Conclusions

Hemicelluloses and cellulose are readily liquefied at lower temperatures in the presence of AcOH. The acid, however, elevates the tendency of condensation reaction of lignin at higher temperatures. The hydrolysis of wood with H-CW in a two-step process can be performed at 10–20°C lower temperatures in the presence of 1% AcOH. The product yields are satisfactory in comparison with experiments without AcOH. The decomposition behavior of the hardwood and

Table 3 Comparison of various saccharides from Japanese beech (*F. c.*) and Japanese cedar (*C. j.*) recovered in monomeric and oligomeric forms as treated by two-step semi-flow hot-compressed water with and without acetic acid (% data based on wt of extractives-free wood flour)[a].

	2-Step treatment without AcOH				2-Step treatment with 1% AcOH			
	Monomer		Oligomer		Monomer		Oligomer	
Saccharide	*F. c.*	*C. j.*	*F. c.*	*C. j.*	*F. c.*	*C. j.*	*F. c.*	*C. j.*
Glucose	4.4 (*15.4*)[a]	5.5 (*16.5*)	24.1 (*84.6*)	27.9 (*83.5*)	11.2 (*40.1*)	10.2 (*22.6*)	16.7 (*59.9*)	34.9 (*77.4*)
Mannose	0.1 (*5.3*)	0.5 (*6.1*)	1.8 (*94.7*)	7.7 (*93.9*)	0.3 (*25.0*)	1.0 (*11.5*)	0.9 (*75.0*)	7.7 (*88.5*)
Galactose	0.1 (*14.3*)	0.4 (*28.6*)	0.6 (*85.7*)	1.0 (*71.4*)	0.2 (*25.0*)	0.5 (*31.3*)	0.6 (*75.0*)	1.1 (*68.7*)
Rhamnose	0.1 (*20.0*)	– (–)	0.4 (*80.0*)	– (–)	0.2 (*33.3*)	– (–)	0.4 (*66.7*)	– (–)
Xylose	1.0 (*4.6*)	1.2 (*21.1*)	20.6 (*95.4*)	4.5 (*78.9*)	2.6 (*12.6*)	2.7 (*32.5*)	18.0 (*87.4*)	5.6 (*67.5*)
Arabinose	0.2 (*40.0*)	0.4 (*50.0*)	0.3 (*60.0*)	0.4 (*50.0*)	0.3 (*50.0*)	0.5 (*71.4*)	0.3 (*50.0*)	0.2 (*28.6*)
Fructose	0.5	0.5	–	–	2.4	1.9	–	–

[a]Italic values in parentheses show relative % based on its total mono- and oligo-saccharide contents obtained in each treatment.

softwood investigated here was different. The efficient utilization of woods for biochemicals and biofuels by means of H-CW treatment needs a lot of optimization in larger experimental units, and feasibility studies are needed to check its economic viability.

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